

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



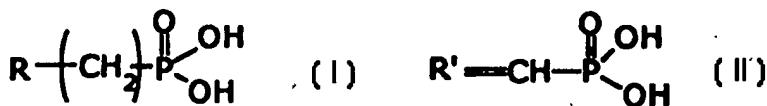
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 8/40, C09D 5/38, C09C 1/64		A1	(11) International Publication Number: WO 99/06450
			(43) International Publication Date: 11 February 1999 (11.02.99)
(21) International Application Number:	PCT/US98/15761		
(22) International Filing Date:	29 July 1998 (29.07.98)		
(30) Priority Data:	60/054,179	30 July 1997 (30.07.97)	US
(71) Applicant <i>(for all designated States except US)</i> :	E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).		
(72) Inventors; and			
(75) Inventors/Applicants <i>(for US only)</i> :	BRUYLANTS, Paul, Peter [BE/BE]; Vinkenlaan 11, B-3191 Boortmeerbeek (BE). HUYBRECHTS, Josef [BE/BE]; Korenblomstraat 39, B-2360 Oud-Turnhout (BE). KIRSHENBAUM, Ken- neth, S. [US/US]; 4160 Wendell Road, West Bloomfield, MI 48323 (US). BERGE, Charles, T. [US/US]; 2948 Mo- hawk Lane, Rochester Hills, MI 48306 (US).		
(74) Agent:	COSTELLO, James, A.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		
Published <i>With international search report.</i>			

(54) Title: PHOSPHONIC ACID REACTION PRODUCTS AND USE IN COATING COMPOSITIONS

(57) Abstract

The invention provides an aqueous coating composition comprising nonionically and/or anionically stabilized film-forming polymers and metallic pigments and a compound which is the reaction product of a phosphonic acid derivative, a hydroxy-functional addition polymers and, optionally a compound having a hydroxy group, in which the phosphonic acid derivative is selected from one or both of (I) and (II), wherein R and R' are selected from the group consisting of an aliphatic and an aromatic substituent having 1 to 25 carbon atoms optionally including heteroatoms of at least one of oxygen, phosphorus and silicon.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakhstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LI	Liechtenstein	RU	Russian Federation		
DE	Germany	LK	Sri Lanka	SD	Sudan		
DK	Denmark	LR	Liberia	SE	Sweden		
EE	Estonia			SG	Singapore		

TITLE
PHOSPHONIC ACID REACTION PRODUCTS
AND USE IN COATING COMPOSITONS
BACKGROUND OF THE INVENTION

5 U.S. 4,675,358 discloses coating compositions employing phosphoric acid derivatives. Such compositions are not very hydrolytically stable. WO 96/08518 describes N-acyl aminomethylene phosphonates and derivatives and their use in waterborne coatings. Such compositions have limited compatibility with other binders and limited durability because of N-containing linkages. EP 391,230

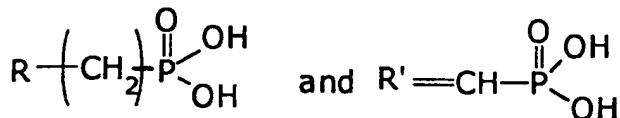
10 discloses compounds which are the reaction product of an alpha-aminomethylene phosphonic acid with an epoxy group of a compound containing at least one epoxy group. Such reaction products have limited end use in water-borne compositions that are anionically stabilized since the amino group destabilizes the coating composition. U.S. 5,151,125 discloses aqueous metallic coating compositions comprising acrylic copolymers to reduce the gassing of aluminum flakes. Such compositions have limited hydrolytic stability and limited effectiveness.

15

SUMMARY OF THE INVENTION

We have found that hydrophobic-substituted phosphonic acid derivatives which are reaction products with hydroxy-functional copolymers are particularly effective for inhibiting the corrosion of metallic pigments in water-borne compositions. The invention concerns an aqueous coating composition comprising a stabilized film-forming polymer, a metallic pigment and a compound which is the reaction product of a, b and optionally c, wherein:

20 (a) is 5 to 95 weight percent of a phosphonic acid derivative consisting of one or both of



wherein R and R' are selected from the group consisting of an aliphatic, cycloaliphatic and aromatic substituent having 1 to 25 carbon atoms and optionally up to 10 heteroatoms of at least one of oxygen, phosphorus and silicon;

30 (b) is 5 to 95 weight percent of a hydroxy-functional addition polymer with a weight average molecular weight of 1000 to 30,000; and

(c) is 0 to 90 weight percent of a compound having one hydroxy-functional group.

Representative examples of phosphonic acid group-containing compounds are vinyl phosphonic acid, propyl and octyl phosphonic acid, and hydroxyethane diphosphonic acid.

Representative examples of hydroxy-functional polymers are addition

5 copolymers of methacrylates, vinylaromatics, acrylates, acrylamides/methacrylamides and their derivatives, acrylonitrile, methacrylonitrile, allylalcohol, maleates, itaconates and vinyl monomers. The copolymers are hydroxy and/or acid functional. Typical comonomers useful to obtain the hydroxy-functionality are 2-hydroxy ethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxy propyl acrylate, 2-hydroxy propyl methacrylate, allyl alcohol, 1,4 butenediol, 4-hydroxybutyl acrylate, bis-hydroxy ethyl maleate and the like. Preferred hydroxy-functional copolymers are copolymers of styrene and allyl alcohol. A preferred phosphonic acid derivative is propyl and octyl phosphonic acid.

10 15 The hydroxy functional copolymers are typically prepared in a free-radical initiated process using peroxy or azo initiators. The reaction between the hydroxy functional copolymer and the vinyl and/or alkyl phosphonic acid can be run in a fusion or solvent process where water is distilled.

15 20 The reaction products of the phosphonic acid derivatives and the hydroxy-functional copolymers are used to treat metallic pigments before the final blend is inverted in water. The final metallic pigment dispersions are stable from gassing.

DETAILED DESCRIPTION

25 Preferred coating compositions are the following:

where the reaction product as corrosion inhibitor is used in the form of a salt;

where the phosphonic acid derivative is propyl, octyl or vinylphosphonic acid;

30 where the hydroxy-functional product is based on a styrene-allyl copolymer;

where the corrosion inhibitor based on phosphonic acid has an acid value of 25 to 400 mgKOH/g;

35 where the composition is anionically or non-ionically stabilized, and where the film-forming polymers are anionically stabilized vinyl, acrylic and/or urethane emulsions.

Preferred phosphonic acid group-containing reaction products are those formed from one or more of vinyl phosphonic acid, propyl and octyl

phosphonic acid, and hydroxyethane diphosphonic acid with one or more hydroxy-functional copolymers of styrene and allyl alcohol. Preferably, R and R' have up to 12 carbon atoms and effect good hydrophobic-lipophilic balance (HLB).

5

EXAMPLES

Example 1

In a reaction vessel fitted with stirrer, thermometer, reflux condenser and Dean and Stark separator, a mixture of 300 parts xylene, 300 parts styrene/allyl alcohol copolymer with a molecular weight of 1600 was heated at 85-90°C till dissolved. There was then added 129.33 parts of octyl phosphonic acid (80% solution in water/ethanol=1/1). The temperature was raised to reflux ($\pm 148^\circ\text{C}$) while water was removed. After 2 hours, 16 parts of water had been removed and the contents of the reactor were vacuum stripped. The reaction product was diluted with 270 parts of 2-butoxyethanol.

15

Test results:

	Solids	58.8%
	Viscosity (Gardner Holdt)	W
	Acid value	148 mgKOH/g
20	Number Average MW	1700
	Weight Average MW	4400

Example 2

Procedure of Example 1 was repeated using 300 parts xylene, 300 parts styrene/allyl alcohol, 215.55 parts octyl phosphonic acid. In total, 28 parts of water were stripped in about 2 hours. After vacuum stripping, the reaction product was diluted in 310 parts of 2-butoxyethanol.

Test results:

	Solids	59.7%
30	Viscosity (Gardner Holdt)	V - 1/4
	Acid value	188 mgKOH/g
	Number Average MW	1300
	Weight Average MW	3800

35

Example 3

Procedure of Example 1 was repeated in which 240 parts styrene/allyl alcohol copolymer were reacted with 73.8 parts of p-tert amylphenol and 137.33 parts of Cublen® K60 in 350 parts of xylene. Cublen® K60 is a 60% solution in

water of hydroxy ethane diphosphonic acid from Zschimmer and Schwarz Company.

Test results:

5	Solids	58.4%
	Viscosity	Y
	Acid value	184 mgKOH/g
	Number Average MW	1560
	Weight Average MW	4260

10 Example 4

Procedure of Example 1 was repeated in which 100 parts xylene, 300 parts of styrene/allyl alcohol copolymer and 85 parts of vinylphosphonic acid were used.

Test results:

15	Solids	59.8%
	Viscosity	Z2
	Acid value	178 mgKOH/g
	Number Average MW	1100
	Weight Average MW	2400

20 Example 5

Styrene/Allylic Alcohol Copolymer Modified with Propyl Phosphonic Acid

Into a 500 ml 3-neck round bottom flask fitted with a reflux condenser, water separator and air-driven stirrer, place the following and heat to 85°-90°C until dissolved:

25	Xylene	50.0 grams
	ARCO SAA100 resin	100.0 grams

Add the following and raise temperature to reflux (~148°C):

propyl phosphonic acid	36.2 grams
------------------------	------------

Continue to heat for 2 to 3 hours when approximately 5.6 grams of water will have been removed by azeotropic distillation. Cool to 100°C and begin vacuum strip to remove about 50 grams of solvent. At the end of the distillation, add the following to the reactor and allow to cool.

Butylcellosolve	90.0 grams
-----------------	------------

Fill out into a plastic container.

35	<u>Product</u>	
	Acid Number	145
	Weight Solids	59%

Example 6

Paint Example:

Parts:

Paint Example:	Parts:
Dispersions	
Passivator Example 2	7.83
Butyl Glycol	58.42
Alu Flake (1)	30.75
Dimethylethanolamine	1.50
Thickener (2)	1.50
Aluminum Based Paint	
Dispersion of Passivator of Example 2	24.03
Latex (3)	27.53
D.I. water	47.55
Defoamer (4)	0.01
Thickener Combination (5)	0.88
Gassing Results (6)	
After 1 week	OK
After 2 weeks	OK
After 3 weeks	OK
After 4 weeks	OK

(1) Stapa Metallic R-607/Eckart

(2) NOPCO DSX 1550/Henkel

5 (3) Latex Anionically Stabilized/DuPont

(4) Balab 3056A/Witco

(5) ASE-60/Polyphobe PP-107 :78/22. Rohm & Haas/Union Carbide

(6) ALU Paint is mixed with iron oxide dispersion and kept in closed container at 49°C.

10

Example 7

Paint Formula:

Parts:

Mineral spirits (boiling range 140-160°C)	4.9
Ethylene glycol-mono-n-hexylether	4.9
Ethylene glycol-mono-n-butylether	10.9
Aluminum Flake (Silverline® SSP-353) (course aluminum flake 70% solids)	17.8
Inhibitor of Example 2	4.3
Acrylic latex 30% in water (Adjust till pH is 9) with aminomethylpropanol	61.5
The gassing was followed by measuring the ml of hydrogen (H ₂) generated in 16 hours at 60°C.	0.90
	5.3 ml

WHAT IS CLAIMED IS:

1. An aqueous coating composition comprising a stabilized film-forming polymer, a metallic pigment and a compound which is the reaction product of (a), (b) and optionally (c), wherein:
- 5 (a) is 5 to 95 weight percent of a phosphonic acid derivative consisting of one or both of



wherein R and R' are selected from the group consisting of an aliphatic, cycloaliphatic and aromatic substituent having 1 to 25 carbon atoms and optionally up to 10 heteroatoms of at least one of oxygen, phosphorus and silicon;

- 10 (b) is 5 to 95 weight percent of a hydroxy-functional addition polymer with a weight average molecular weight of 1000 to 30,000; and
- (c) is 0 to 90 weight percent of a compound having one hydroxy-functional group.

- 15 2. A composition of Claim 1 where the reaction product is in the form of a salt.
3. A composition of Claim 1 where the phosphonic acid derivative is propyl, octyl or vinylphosphonic acid.
4. A composition of Claim 1 where the hydroxy-functional product is 20 based on a styrene-allyl alcohol copolymer.
5. A composition of Claim 1 where the corrosion inhibitor based on phosphonic acid has an acid value of 25 to 400 mgKOH/g.
6. A composition of Claim 1 where the film-forming polymers are selected from anionically stabilized vinyl, acrylic and urethane emulsions.
- 25 7. A composition of Claim 1 where the phosphonic acid group-containing reaction products are formed from one or more members selected from the groups consisting of vinyl phosphonic acid, propyl phosphonic acid, octyl phosphonic acid and hydroxyethane diphosphonic acid with one or more members selected from the group consisting of hydroxy-functional copolymers of styrene and allyl alcohol.
- 30 8. A composition of Claim 7 comprising copolymers of styrene/allyl alcohol and propyl phosphonic acid.
9. A composition of Claim 1 which is anionically stabilized.
10. A composition of Claim 1 which is nonionically stabilized.

INTERNATIONAL SEARCH REPORT

Int	tional Application No
PCT/US 98/15761	

A. CLASSIFICATION OF SUBJECT MATTER	IPC 6 C08F8/40	C09D5/38
		C09C1/64

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09D C08F C09C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 319 971 A (PPG INDUSTRIES INC) 14 June 1989 ---	1
A	EP 0 401 833 A (NAT STARCH CHEM INVEST) 12 December 1990 ---	1
A	US 5 637 441 A (BRENNK MICHAEL ET AL) 10 June 1997 see column 3, line 49 - column 4, line 11 ---	1
A	US 5 429 674 A (LAMERS PAUL H ET AL) 4 July 1995 cited in the application ---	1
A	EP 0 391 230 A (PPG INDUSTRIES INC) 10 October 1990 cited in the application ----	1

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

2 November 1998

11/11/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patenttaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Miller, A

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/15761

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 0319971	A 14-06-1989	AU 2668188 A JP 1190765 A		06-07-1989 31-07-1989
EP 0401833	A 12-12-1990	US 5023368 A CA 2017786 A,C DE 69003013 D DE 69003013 T US 5126108 A		11-06-1991 08-12-1990 07-10-1993 20-01-1994 30-06-1992
US 5637441	A 10-06-1997	DE 4423140 A BR 9503065 A DE 59501625 D EP 0689941 A ES 2113696 T JP 8058264 A		04-01-1996 11-06-1996 23-04-1998 03-01-1996 01-05-1998 05-03-1996
US 5429674	A 04-07-1995	AT 166072 T AU 3330795 A CA 2199170 A CN 1157622 A DE 69502506 D EP 0781298 A ES 2116759 T JP 9511778 T WO 9608518 A		15-05-1998 29-03-1996 21-03-1996 20-08-1997 18-06-1998 02-07-1997 16-07-1998 25-11-1997 21-03-1996
EP 0391230	A 10-10-1990	US 5034556 A AT 138952 T AU 617245 B AU 5213490 A CA 2012684 A,C CN 1046165 A DE 69027250 D DE 69027250 T ES 2090055 T JP 2577529 B JP 6340825 A JP 2290890 A JP 2568728 B MX 169220 B		23-07-1991 15-06-1996 21-11-1991 04-10-1990 03-10-1990 17-10-1990 11-07-1996 02-01-1997 16-10-1996 05-02-1997 13-12-1994 30-11-1990 08-01-1997 24-06-1993

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/15761

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0391230 A	US 5091451 A	25-02-1992	